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Environmental Degradation of Materials

Lecture – 23
Broad Subject: Forms of corrosion, Uniform corrosion, Galvanic corrosion

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So you see that there are several issues which are falling under metallurgical factors which can govern corrosion rates. Now we have environment related factors, in case of environment related factors there are mainly three subsections, one is concentration, concentration cell this sort of problem arises in case of localized attacked or rainwater, rain droplet related attack. For example, on a particular body this is a metal, on that metal if one side is depleted in oxygen and another side is excess of dissolved oxygen, so this is more dissolve oxygen and this part is depleted, depleted that case this part will act as cathode, and this part will act as anode, and so this section there will be corrosion and this is happening because the change in concentration of dissolved oxygen. So we are forming a concentration cell where this part is cathode, this part is an anode.

And so the anodic part, this part will corrode and this part would be protected since the cathodic reaction will happen on this metal surface of this section. So this is an example of concentration cell formation, we will talk about this when will discuss the pitting or crevice corrosion.

Now there could be another issue which is a velocity related problem, velocity of the corrosive, the electrolyte depending on the velocity of the electrolyte, there could be change in corrosion phenomena the same corrosion phenomena let's say the pitting, if we have low velocity if we have a stagnant solution or in case of crevice, if we have stagnant solution the formation of pitting or crevice corrosion would be aggravated, okay but if we increase the velocity there could be a possibility of very low amount of crevice corrosion or pitting corrosion, but if we increase velocity it may happen that after reaching some critical velocity there could be more amount of erosion corrosion, so velocity is another factor.

Now there could be a factor of temperature, more or less if we increase the temperature the rate of any reaction increases, but and in all the cases, most of the cases if we increase the temperature the corrosion rate increases, but there could be some examples where there could be a reversal of polarity, and one such example is if we have steel iron and zinc, iron zinc if we have coupling and then below certain temperature iron will act as cathode, zinc will act as anode, and on zinc surface zinc hydroxide will form below certain temperature but if we increase the temperature of the system then the zinc hydroxide will convert to zinc oxide, instead of zinc hydroxide zinc oxide will form on the zinc surface and zinc oxide is cathodic to iron, so that case iron will corrode zinc will be protected, since zinc oxide layer has formed above some critical temperature and that gives to corrosion of iron instead of protection, so the temperature is another issue, okay, so if we increase the temperature most of the cases the corrosion rate increases, but there could be a possibility of polarity reversal due to the formation of different passive layer, so this is another factor, this is temperature factor.

Now if we consider metallurgical and environment factor together we'll have, we can explain many failures due to corrosion. There is one more important factor that is stress or pressure related factor, stress or pressure. Now most of the cases our engineering components are under stress so if we have stress at the same time if we have corrosion phenomena combinedly we can have corrosion fatigue, we can have hydrogen embrittlement, we can have stress corrosion cracking all sort of problems can arise.

Now what is about the pressure? Now pressure for example in case of fretting corrosion, okay, in case of fretting corrosion we have seen that two components are under compressive stress and there is a very minor scale of scale or relative movement between these two components and in the contact area we have corrosion problem, with that problem is called fretting corrosion and that time it is not the tensile stress is rather the compressive stress and the relative movement or the vibration of the components with respect to each other that leads to corrosion, that is pressure related problem. And also you can have another factor that is, if we have a difference in pressure, for example in case of profiler, in case of propeller one side is having higher pressure, one side is having lower pressure, other side is having lower pressure, so the higher side will have more corrosion compared to the lower, if we have this part so this part is high pressure, and this part is low pressure.

Now when we increase the pressure, we only decrease the pressure of water there is a possibility of bubble formation, now at the same time if we on the cyclic process if we increase the pressure at that point then bubble can collapse, so we have seen this bubble is forming and if we increase the pressure bubble is collapsing and this formation and collapse this particular, these two phenomena, these two phenomena, phenomenon, phenomena they can happen simultaneously and lead to a cavitation problem, cavitation damage, so pressure is another important issue, stress is another important issue, clubbing with the corrosion phenomena.

So we see that there are major three factors, one is metallurgical, another is environment related, another is a stress and pressure. Now we have two special corrosion phenomena, one is called microbial corrosion, another is liquid metal corrosion. Liquid metal corrosion or liquid metal embrittlement, liquid metal embrittlement, we'll talk a little about this microbial corrosion and liquid metal corrosion as we go ahead.

Now once we have discussed about the different forms of corrosion in short and also the factors which can govern all those forms of corrosion. Now let us get into the individual forms of corrosion, now first which is coming in the list that is uniform corrosion. Uniform corrosion the name suggests that there should not be any localized attacked rather on a particular metal object the corrosion would be uniform throughout the entire cross-section or the section surface of the particular structure, for example our car body, example is car body structure, car body corrosion or there are several other examples for example tarnishing of silverware, for example silver bowel and all those stuff or the silver ornaments they do get a blackened, okay, as we use them, so this dark fair black part is nothing but the most of the cases it's AG_2S, so that AG_2S can lead to tarnishing which basically changes the texture or lustier or the changes the shininess the silverware.

Now there could be other example rusting of steel in air, or corrosion of structural steel. Now if you see when a body is exposed to atmosphere there is a possibility of a uniform corrosion all throughout the section, now if you consider particular this example, the equations that govern corrosion we can see that gradually there are few equation, for example one is iron goes to iron + 2 ion, so this is the anodic reaction, what is the cathodic reaction in atmosphere? The atmosphere this is anodic reaction and atmosphere we have oxygen and it's almost close to neutral media so H_2o + 4e goes to 4 OH^-, this is the cathodic reaction. Now these two can react forming $Fe(OH)_2$, now once we have a $Fe(OH)_2$ it can further react with the oxygen that is there in the atmosphere that oxygen reaction along with presence of moisture it can go to 4 $Fe(OH)_3$ so this is hydrated ferric oxide or $Fe(OH)_3$ even we can directly get Fe to hydrated Fe_2O_3, $4Fe(OH)_3$ + once that it reacts with oxygen and go to 2 Fe_2O_3 H_20 so plus $2H_2O$ so this is nothing but the rate rust what we see on the structural steel, so this is, this reaction Fe + 2 and this reaction if we have the structure all over the places these reactions are happening and all over the places corrosion rust is forming. So this is and gradually you have the cross-sectional changes because this rust might get detached from the surface so gradually you will see that you have this much which is left out after a long time.

Now how to avoid this particular corrosion, this is a very general corrosion phenomena and the protection one sort of protection is since you cannot avoid corrosion, so one protection is you, in the beginning instead of having this exact dimension we will have a little extra material in it so that extra material will take care of that material loss due to uniform corrosion.

Now second thing is we can go for cathodic protection, so what are the protection mechanism, protection we can employ in case of uniform corrosion, protections are one is extra material we have the dimension would be little higher just to take care of this uniform corrosion, second is you can have cathodic protection, paint will work nice here, painting would be great in case of taking care of this or controlling the uniform corrosion, so these are the methods, common methods which can protect this uniform corrosion.

Now what are the factors? Now if you see that the factors are very clear presence of moisture, so humidity is important factor, humidity is important factor second case let say tarnishing of silverware there we form AG_2S, so AG_2S so that means the presence of H_2s or SO_2 in the atmosphere that can decide whether the silverware will corrode faster or not even in the presence of SO_2 there could be a reaction, there could be extra corrosion of iron object because the SO2 can dissolve in moisture and it makes it acidic because there could be a sulphuric acid formation, okay, so that sulfuric acid media iron can get corroded at a little faster rate.

Now third is due, now if there is a due formation then the possibility of uniform corrosion increases and if it is a dry place then the uniform corrosion would be less, so these are the major factors which guide of course other factor is temperature, temperature or presence of salt mainly NACL let say metal or structured is exposed to media or environment where we have lot of NACL content, let say which the structure is near to the seashore so there since we have salt, the salt always agree with the corrosion phenomena.

Now again if we have a cold place and a hot place, the hot place in the presence of all these factor, other factor there could be extra corrosion, if there is no due formation, if there is dry place then the corrosion rate would be less or if it is a wet place corrosion rate would be more, so these are the common factors which guide uniform corrosion. So this is about uniform corrosion but the more important corrosion phenomena would be the localized corrosion, okay, so the localized corrosion that may arise, the first example we would give that is the galvanic corrosion, where the uniform corrosion in fact another important issue is in case of uniform corrosion we can predict what could be the life of that particular structure, greatly predict but if it is it is localized corrosion most of the cases localized corrosion are very difficult to detect by normal naked eye observation, so those corrosion phenomena are to be looked at very carefully and studied properly.

So let us get into a first example in for localized attacked, first example of localized attack is galvanic or two metal corrosion. So the galvanic and two metal corrosion is very, very common form of corrosion and since one particular metal you cannot make use it for structural applications most of the time you need to use many different metals or alloys into your structure, so that case when you use it that time you have to join all those different parts, so when you go for joining that time you definitely need to have a two metal contact and if that two metal contact we exposed to electrolyte or corrosive then there could be a possibility of galvanic corrosion or two metal corrosion. For example, if we have stainless steel, if we have stainless steel and then that stainless steel is connected to normal mild steel then we have a galvanic contact around at this zone, so at this zone and stainless steel will act as and in case of let say normal atmospheric corrosion or sea water corrosion, stainless steel will act as cathode and mild steel will act as anode, fine, so the mild steel part will be corroded faster than the corrosion of stainless steel part. So this is basically an example of galvanic corrosion, so these sort of phenomena can arise if we have two different metals in contact and one metal will act as cathode and another metal will act as anode, and the metal which will act as anode that would be active in a particular series and the cathode material will be acting as noble metal in the particular series.

Now I am talking about a series, that series is called galvanic series, and this galvanic series for a particular solution let say NACL solution or seawater solution and which is unpolluted seawater solution there if we dip, let say this is my seawater solution and if we dip a particular metal object M it will have its own free corrosion potential, so if you measure the corrosion potential with a reference electrode, with a reference electrode we can see that at a particular potential it stabilizes most of the cases and that corrosion potential is called free corrosion potential with respect to mixed potential theory if it is log I versus potential plot if we do that time we will see that cathodic line, polarization line and anodic polarization line they are cutting at a particular point which is basically the equilibrium point, where the rate at which cathodic reaction happens would be equal to the rate at which anodic reaction goes on. So this is my free corrosion potential, free corrosion potential and if we do polarization experiment we will see that the graph will look like this. So now for a particular metal M, let us say the free corrosion potential is E1.

Now another metal which is let us say this is for M1, M1 free corrosion potential is or the corrosion potential is E1 in this particular sea water solution, now another metal if we take M2 where the free corrosion potential is E2, now if E1 is greater than E2 and M1 and M2 this two metal part is connected or welded or braised at this point or welded at this point and then if we expose this to seawater then this one will act as cathode and this one will act as anode, since E1 is greater than E2 the reverse reduction potential E1 is greater than E2, so this one will be noble in the particular series and this one will be active in the particular series. So if we would like to put it in the galvanic series then M1 would be on top and M2 would be below this M1. So now in this case we have also seen one more series that is electrochemical series, that series if you see there only the pure metals are put there in that particular series according to their reversible reduction potential in non-corroding position or non-corroding situation, so then also you will see that, that case you always see some reduction potential number, let us say if we have reduction EMF series or electro-motive force series and if it is the reduction potential if we consider M+N/M the reduction potential then you will see that this H+ E H, this has potential 0V with respect to hydrogen reference electrode. And also you can see that the Zn++/Zn there the reduction potential would be - 0.761V, so and also if you see Cu++/Cu there also you will see E0 would be equal to 0.34, this is plus, this is minus, and this is 0. So according to this EMF series we see that the copper pure metal, copper will be noble compared to the pure zinc and that situation is arising when that is non-corroding this situation that means zinc ion concentration would be 1 or the activity of the zinc ion is 1 and there is no other elements, no other species, but this situation is more or less ideal situation since most of the cases we deal with alloy systems and another situation most of the cases we don't deal with the element concentration which is one activity, most of the situation they are away from this one activity or even the situation may arise that element, that elemental ion is not present in the corrosion, so how to get some idea that which one would corrode and which one would not corrode that would give, would be given by galvanic series, this can give you the idea if those are pure and if we club copper and zinc, copper would definitely not corrode rather copper deposition will happen and zinc would corrode.

But now in case of this situation here all those numbers are there, but in case of galvanic series we have to just see what is the relative behavior of all those metals or elements or different species, corrosive species for example oxygen, dissolve oxygen all those species what is basically the relative position as per the free corrosion potential in a particular solution, let us say in case of NACL unpolluted solution iron will be placed, mild steel will be placed like this and in that situation the stainless steel 18:8 stainless steel will be on top of this and you will not find any value of potential, any value of potential is just the relative position in case of NACL solution, and in case of galvanic series the metal which has higher position than the mild steel that is actually the noble metal compared to the other metal, so if you club this two and if we have a galvanic coupling between 18:8 stainless steel and mild steel then always this will not be corroded, this will corrode, so this is the essence of galvanic series, like that you can place all the metals as you want to have the information of different metals and alloys you can form a galvanic series.

Now another situation is for example copper, let us say I have copper and I have a steel, mild steel, so I have copper and mild steel, this is a copper plate, and this is mild steel plate, now if we would like to see what happens in case of seawater situation, that situation this will act as noble and this will act as active and if we would like to take it to this situation then of course in the particular series copper will be placed at top and mild steel would be placed at the below this copper, so this is the position of copper and mild steel in the galvanic series in NACL solution. So if we have this situation, this will corrode, this will not corrode and this will act as cathode, and point is that situation you don't see any copper iron or iron ion as you have in case of EMF series.

Now what are the reactions then in case of mild steel scene since this is anode, so always iron will release two electrons and it will go to Fe++ ion and it will dissolve, but what would be the cathodic reactions? Since these two electrons are to be supplied, are to be consumed, so who will consume that? So cathodic reaction would be since seawater, we have dissolve oxygen and seawater is neutral in nature, so oxygen in the presence of H2O except this 4 electrons and goes to 4OH -, so this is the cathodic reaction which will happen on this, so as we already have seen that the surface on top of which cathodic reaction happens that is nothing but getting protected. So this will protect, this will be protected and this will be corroding, so this is the essence of galvanic series we can have a long series like this, now this is of course the solution dependent if we change the solution, the situation can vary one particular metal for example M1 and M2 example in that situation in NACL if it is M1 is anode, M1 is sorry, M1 is noble, M2 is active, in different solution it may arise that M1 could be active, M2 could be noble, so that is what you can have infinite number of series and different solutions, so what are the characteristics of galvanic series, since this galvanic corrosion or two metal corrosion depends on that galvanic series characteristics, so let us see the characteristics, one is position of metals and alloys in the galvanic series agree closely to their constituent elements in the EMF series more or less it happens, so if copper is noble, zinc is active, so in case of alloy system also copper will act as noble, and zinc will act as active, but this is not sacrosanct this may vary, okay, so position of a particular metal is basically closely related to EMF series.

Now second case passivity might or passivity always changes the position of the noble and active nature of the particular metal, for example 18:8 stainless steel and MS, both the major component is iron, fine, but the iron component here we have chromium around 18% chromium so because of this presence of 18% chromium there could be a possibility of formation of chromium oxide passive layer, and once chromium oxide passive layer forms that chromium oxide passive layer acts as cathodic in comparison to a normal iron or mild steel, so since we have 18% chromium and it is passive so this will be acting as noble and this will be acting as cathode, is acting as active, if this will be active metal in the couple between mild steel 18:8 mild steel and 18:8 stainless steel with mild steel, so this is passivity of course changes the position of different metals in the series, then we have in the galvanic series if you see carefully in a book then you will see some of the galvanic series, for example let me put an example, let us say 18:8 molybdenum stainless steel, then 18:8 stainless steel and both are in active state. Now this you can see in the book it is in bracketed, now there are two issues, one is why there is a bracket, and why I have written active here, now before until unless the passive layer forms it cannot behave as passive metal, so the passivity depends on the solution as well as until and unless the passively formed it will always act as active, so that is what when it is in active state then this two cases, these two metals will always behave similarly in that particular solution, similarly means both will have of the same level of free corrosion potential. So if they have same level of free corrosion potential if we combine them then there would be a very little potential difference between this two couple and if there is a very little potential difference so there the situation will not be a galvanic in nature there could be uniform corrosion over the two different metal surfaces. So that's what this bracketed and this active means they have not gone into passive state.

Now similarly we can have another bracket which is 18:8 molybdenum stainless steel where it is passive and 18:8 stainless steel, SS means stainless steel passive, so there also you will see a bracket, it means that these two metals or these two alloys will act similarly if we contact them if we make a contact out of this two different alloy systems, so and both the cases they have reached to the passive state, so that's what if we combine them club them then there could be a less effect of galvanic, galvanic effect would be less since the pre-corrosion potential in the particular galvanic series or the solution is same for both the cases, if they are almost same so the potential difference would be less or very small and since the current, the corrosion is decided by the rate of current flow or the rate of electron flow or the current density and if they have a similar potential level so there would be less amount of galvanic coupling or galvanic effect and so the corrosion rate would be same for both the cases, so that is what they are put it as a bracketed, so this is the meaning of bracket in the galvanic series, so we see that in the galvanic series we have the bracketed regions and in practical use this has a great implication so in those bracketed metals and alloys they can be clubbed together in practical operation without having much of galvanic corrosion effect, so uniform corrosion always would be better so there we can have uniform corrosion if we combine all those metals with the bracketed regions, bracketed metals and alloys in the galvanic series, so this is, these are the characteristics of galvanic series.

Now let us get into some of the practical examples of galvanic corrosion, one example is definitely a yacht with monel hull + steel rivet, so if you have the monel hull and steel rivet, the monel hull can lose structure and it cannot operate for a long period, since monel hull will be cathodic and steel rivet would be anodic and there is one particular issue that is governing there, that is the area factor, we will talk about that area factor, this is a major problem if we have steel rivet and monel hull then the steel rivet cannot hold, cannot give strength to the monel hull for a longer period it will lose strength.

Second is same way the copper plate, copper plate which is fastened with steel rivet or steel bolt that is also a very, very bad practice, still copper plate will lose its strength.

Third one is an example of tank, water tank so let us, this is the water tank and initially this is made with mild steel and the corrosive, the solution or the electrolyte is mildly corrosive but in order to protect, in order to have further protection if we put a stainless steel bottom, if we put stainless steel this is stainless steel, and this is mild steel that case this part where we have welding between stainless steel or the cladding of stainless steel with the mild steel on top that part will, can develop lick or so the metal the solution can go out through this lick, so this is another example.

So now we see all those examples, now until and unless we see what are the factors those are important in case of galvanic corrosion we cannot explain much about this we see all those observations, now the factors if we see there are three major factors, one is environment effect, environment factors, second is area ratio, area ratio means cathodic area and anodic area. Third one is distance effect, now if you see the environment affect, environment affect for example temperature, it could be moisture, it could be salt content of the electrolyte, salt means NACL of the chloride salt, those are the three factors which can be deleterious to the material and the corrosion would be more.

Now as we are discussing about the temperature effect, let us say we have iron on top of that if it is a galvanized, so galvanized means zinc coating and let us say some part of this galvanized coating is damaged so that case since zinc is active in the series compared to iron, so iron will act, iron surface, this iron surface will act as cathode, so cathodic reaction which is nothing but O2 plus in normal atmosphere O2 plus or seawater $O_2 + H_2O + 4e$ it forms 4 OH, this is cathodic and anodic reaction will happen, anodic reaction since it is anodic reaction there would be zinc corrosion, and this Zn^{++} will react with OH^- it will form zinc hydroxide. Now if zinc hydroxide is forming that will be on the surface and it would be a loose powder and still this will act as cathode and this will act as anode and this will be cathodically protected.

So we see that zinc hydroxide is forming, now this process that protection of iron cathodically protecting cell protected and zinc corrosion this phenomena will go on till 180 degree Fahrenheit, now if it is more than 180 degree Fahrenheit the situation will be different, that case instead of zinc hydroxide, zinc oxide will form and this is a very adherent layer on the zinc surface. Now once we have zinc oxide on top of this, zinc oxide is cathodic compared to iron, then iron this surface will act as anode and this one will act as cathode, so if zinc oxide surface that means the zinc oxide is forming on top of this if that is cathode and this is anode so the corrosion will happen in this part, so we will not get any protection, so this process is dependent on temperature and this is happening because there is a reversal of polarity, what does it mean? Initially iron was cathode, now after the temperature has reached beyond 180 degree Fahrenheit so this has become anode, so this polarity difference can lead to corrosion to the material which is subjected to corrosion protection, because of the zinc coating.

Now this is temperature factor, another issue is moisture if there is moisture of course then you have always a thin layer of electrolyte on the surface, if there is, if it is a dry place let us say this is dry and this is moist, so in the moist case if we have a metal object and dry place if you have a metal object on the moist surface there is a thin layer of moisture on top of the metal, but here you don’t have, so you have the presence of electrolyte and that case if we have a galvanic couple M1 and M2 then as per if the M1 is on top of the M2 in the galvanic series then M1 will not corrode, M2 will corrode, so the galvanic effect would be more vigorous if there is a moisture.

Now salt content of course again salt increases the conductivity of the electrolyte, so if it increases the conductivity so that there will be easy current flow and easy in current flow means there could be more corrosion, now it can be explained on the basis of mixed potential theory we see that if we draw a mixed potential plot log I versus potential, this is my corrosion point, this is my I Corr, this is my E Corr.

Now if there is no resistance that means the electrolyte is highly conducting then the situation would be like this, if the electrolyte is not that conducting, if there is resistance to the flow of ions then we have resistance drop or resistance polarization, these resistance polarization is measured as IR drop, if there is IR drop then my corrosion current or the current density corresponding to anodic dissolution is from here to here, so initially it was here when it was highly conducting the electrolyte was a highly conducting, but in this case the electrolyte conductivity has reduced or other way around electrolyte resistance has increased and there is IR drop and so the current density corresponding to IA has decreased ,so the corrosion rate has also decreased, so this is a galvanic effect will also be less if we have less salt or the moisture the electrolyte is highly resistant. Now that's what if we have galvanic couple M1 and M2 and on top of that if we have a electrolyte and that will let us say that electrolyte is pure water and that pure water is deionized, in case of deionized water resistance is pretty high so that case galvanic corrosion effect or the corrosion rate would be more or less, pretty low compared to the case where the electrolyte contains lot of ions.

Now in this case another situation can arise that is the distance effect, now let us say this is the contact point between M1 and M2 metal, now the galvanic couple, actual coupling is here, now as you go away from this what happens, the ions has to move, ions have to move a longer distance, so if the ion is moving like this, like this, so longer distance it always leads to pass through the resistant path, so the corrosion effect would be more near the junction and away from the junction since it crosses hired resistant path that IR drop would be more in these situations so the corrosion would be less in this situation and this case if we follow this particular diagram M2 would be cathode, and M1 would be anode, since I am showing the corrosion effect on the metal surface which is active in nature. So the distant affect is also important, so close to the joint the corrosion effect would be, galvanic effect would be more and away from the joint galvanic would be, galvanic effect would be less in case of the active metal in that particular couple. So this is environment factor, this is distance effect.

Now the more serious factor which is the area of ratio or the ratio between the cathodic part and the anodic part, the area factor between these two particular sections, let us say this M1 and M2 if those are the same area then the galvanic effect would be there, but it will not be that serious but if the situation is like this if M1 is active, and M 2 is noble, and M2 has larger area compared to the M1 then the situation would be very different and M1 corrosion rate would be many fold compared to those, this situation where the areas are same.

Now why this happens, we have already explained this with respect to the mixed potential theory, let me also just briefly talk about that then we will take care of this, we will explain this three phenomena.

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